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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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R C van Dijk



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SigmaKalon Services B.V.
Amsterdamseweg 14
1422 AD Uithoorn
PAYS-BAS

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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
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Process for the preparation of poly/silyl ester)s, and their uses

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**PROCESS FOR THE PREPARATION OF POLY(SILYL ESTER)S,
AND THEIR USES**

The present invention relates to a new method for the
5 preparation of poly(silyl ester)s. The invention further
relates to novel poly(silyl ester)s, and in another
aspect, the invention further relates to the use of
hydrolysable poly(silyl ester)s where the use of
hydrolysable silyl ester groups is advantageous.

10

Poly(silyl ester)s possess a variable yet predictable
degradation behaviour and as such, have a broad range of
potential applications wherever the presence of
hydrolysable groups is advantageous. For instance, it is
15 known to use degradable polymers in general in the
medical, environmental, biomedical, and agricultural
areas, wherein the ability of the polymers to break down
into biologically or environmentally resorbable small-
molecule byproducts is of great use.

20

Another application is as a resin or co-resin for self-
polishing antifouling paints, for instance, as binders for
modern antifouling coatings, although the use of
hydrolysable poly(silyl ester)s, as noted above, will have
25 many applications where the fact that the degradation
behaviour can be affected by the nature of the
functionality attached to the silicon atoms would be a
positive advantage.

30 Trialkylsilylcarboxylates of aliphatic carboxylic acids
can be obtained by transesterification. H.H. Anderson et
al describe in J.Org.Chem 1716 (1953) the reactions of
triethyl silyl acetates and diethyl silyl diacetates with

halogenated propionic acids and in J.Org.Chem. 1296 (1954) the reactions of dimethylsilyl di(trifluoro acetate) or dimethylsilyl dipropionate with chloroacetic acid; they distill the acetic, propionic or trifluoroacetic acid
5 under reduced pressure.

Russian chemists (Izv.Akad.Nauk.Ussr.Ser.Khim. 968 (1957)) run similar reactions but at much higher temperatures (190-210°C).

10

JP 95070152 A discloses reactions of trialkylsilylacetates with C6 to C30 carboxylic acids (e.g. palmitic, myristic, benzoic,...); the acetic acid is distilled under reduced pressure or azeotropically with hexane.

15

Poly(silyl ester)s are characterised by the fact that they comprise more than one silyl carboxylate unit in the oligomeric/polymeric backbone. In other words, poly(silyl ester)s contain -Si-O-C(O)- linkages along the polymer
20 backbone, and are a class of degradable polymer systems with a variable, yet predictable, degradation behaviour.

Silyl ester functionalities have been prepared by many routes and therefore it may have been envisaged that the
25 synthesis of poly(silyl ester)s would be relatively straightforward. However, problems such as salt formation, side reactions, monomer insolubility/impurity, and/or incomplete reaction, ensured that many of the envisaged polymer syntheses were not in fact suitable.
30 Indeed, it is only recently that the incorporation of acyloxysilane groups in a polymer backbone has actually been achieved.

Woolley et al have developed and disclosed synthetic routes for the preparation of poly(silyl ester)s, including transsilylation esterification of AA/BB comonomers (see Macromolecules (1995) 28 8887; Macromolecules (1998) 31 7606; J.Polym.Sci., Part A : Polym.Chem. (1999) 37 3606; Macromolecules (1998) 31 15; and J.Organomet.Chem. (1998) 542 235), transsilylation esterification of AB monomers (see Macromolecules (2000) 33 734; and J.Organomet.Chem. (1998) 542 235), hydrosilylation of AB monomers (see Macromolecules (2000) 33 734), and cross-dehydrocoupling polymerisation of AB and AB₂ monomers (see Macromolecules (2001) 34 3215, and references cited therein).

For example, the transilylation ester interchange reaction of chlorosilanes with TMS-blocked silyl esters at temperatures in the range of 100-135°C for 10-14 days, leading to the formation of corresponding polymers with the concomitant distillation of trimethylsilyl chloride, using, for example, N,N-dimethylformamide (DMF) as a catalyst, has been described by Woolley et al, in Macromolecules (1998) 31 15. This method does have its advantages; no base is required, and the trimethylsilyl chloride by-product is volatile. Moreover, the reaction proceeds at relatively low temperatures, and without the addition of a solvent. However, TMS-blocked silyl esters are expensive reagents and the release of trimethylsilyl chloride is harmful to the environment.

Another method described by Woolley et al in Macromolecules (2000) 33 734 and Macromolecules (2001) 34 3215 is the polymerisation accomplished via hydrosilylation between a silyl hydride function and a carbon/carbon double bond or a carboxylic acid function present in the same molecule

(AB monomer system) or in different molecules (AA/BB monomer system). This method suffers from the disadvantages of requiring the use of transition metal catalysts such as platinum or palladium derivatives
5 (Pt(COD)Cl₂;Pd/C) in order to generate hydrogen when carboxylic acid functions are involved and the limited accessibility of the starting materials.

Therefore, there remains the need to find a novel method
10 for the preparation of poly(silyl ester)s avoiding or at least alleviating the aforementioned problems associated with the prior art methods of synthesising hydrolysable poly(silyl ester)s.

15 Therefore, an object of the present invention is to provide a novel process capable of readily preparing poly(silyl ester)s in a high yield from easily and readily available starting materials.

20 Another object of the present invention is to provide a more efficient process for the preparation of poly(silyl ester)s compared to those previously disclosed methods discussed above.

25 A further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s which proceeds at an acceptable rate even without the presence of any added catalyst.

30 A yet further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s wherein only harmless and easily distillable molecules are released.

5

A yet still further object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s wherein the degree of conversion of the starting materials to the target product may be monitored by conventional analytical tools and/or by determining the amount of distilled molecules released.

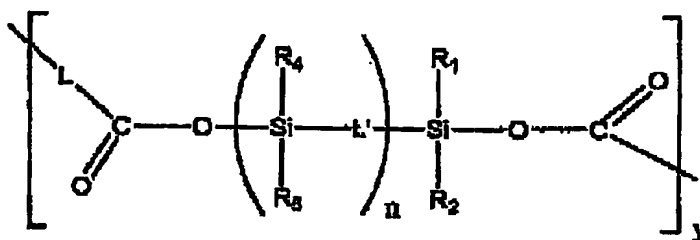
Thus, overall, the object of the present invention is to provide a novel process for the preparation of poly(silyl ester)s offering some improvement vis-a-vis the disadvantages disclosed hereinbefore.

The present invention is based on the reaction of polyacids (and by "polyacids" we mean an organic moiety comprising at least two acid groups; for example at least two carboxylic, sulphuric, phosphoric, and the like, acid groups; preferably, we mean polycarboxylic acids) with polyacyloxy silyl derivatives to synthesise poly(silyl ester)s by silyl ester transesterification. The use of polyacids and the technique of transesterification in the synthesis of poly(silyl ester)s was unexpected as hitherto, the technique of transesterification had only been used to synthesise organosilylated carboxylate monomers, and previously disclosed methods of synthesising poly(silyl ester)s were either found to be ineffective at polymer formation or used expensive reactants and/or produced harmful by-products and/or required an added catalyst and/or could not be followed easily by conventional analytic tools.

6

The present inventors have surprisingly found that by reacting polyacids with polyacyloxysilyl derivatives, poly(silyl ester)s could be synthesised.

- 5 According to a first aspect, the present invention relates to a new process for the preparation of poly(silyl ester)s comprising a structural unit of the formula (I)



10

(I)

wherein each R_4 and R_5 may be hydroxyl or may be independently selected from alkyl, aryl, alkoxyl, aryloxy, $-\text{L}'-\text{SiR}_1\text{R}_2-$, $-\text{L}'-(\text{SiR}_4\text{R}_5\text{L}')_n-\text{SiR}_1\text{R}_2-$, alkenyl, alkynyl, aralkyl or aralkyloxy radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxy, hydroxyl, aryl, aryloxy, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R_4 or R_5 may independently be an $-\text{O}-\text{C}(\text{O})-\text{L}-$ group,

wherein each R_1 and R_2 may independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxy, aralkyl or aralkyloxy radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxy, aryl, aryloxy, halogen, hydroxyl,

7

amino (preferably, tertiary amino) or amino alkyl radicals, or R_1 or R_2 may independently be an $-O-C(O)-L$ -group,

5 wherein L represents a hydrocarbyl or substituted hydrocarbyl group, wherein said substituted hydrocarbyl is substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, hydroxyl, halogen,
10 amino or amino alkyl radicals, or a polymer with pendant acid groups,

L' represents O, S, or NR_6 , where R_6 is defined as is R , below, or L ,

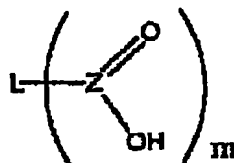
15

each n independently represents a number of $-Si(R_4)(R_5)-L'$ - groups from 0 to 1000,

and y represents a number of silyl ester repeat units from
20 2 to 100000, more preferably 2 to 10000, most preferably 2 to 1000,

which process comprises the step of reacting;

25 a polyacid of formula (II)



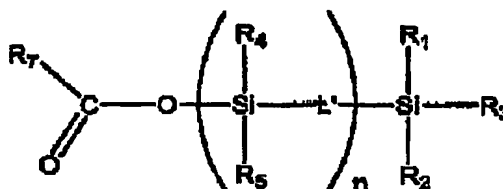
(II)

30

8

wherein Z(O)OH represents the acid moiety attached to I, m is an integer from 2 to 100000, preferably 2, and L is as defined above, with a polyacyloxysilyl derivative of formula (III)

5



(III)

10 wherein R_1 , R_2 , R_4 , R_5 , L' and n are as defined above, except R_1 , R_2 , R_4 and R_5 in (III) are $-O-C(O)-R_8$, where R_8 is defined as is R_7 below, when the equivalent group in (I) is $-O-C(O)-L-$, and R_7 is a hydrogen atom, an aralkyl, aryl, alkenyl, alkynyl, or alkyl group optionally
15 substituted with one or more substituents selected from the equivalent substituents as defined for R_1 , R_2 , R_4 and R_5 above,

and R_3 is the group $-O-C(O)-R_9$, where R_9 is defined as is
20 R_7 above,

whilst removing the formed acid group(s) of formula (IV) and (V),

25 R_7 Z(O)OH (IV),

R_9 Z(O)OH (V),

from the system.

Essentially, it is required that the polyacyloxysilyl derivative is such that there is more than one acyloxy group attached to one or several silicon atoms. Moreover, when $n=0$ there are a maximum of four acyloxy groups on the silicon atom; and when $n>0$, the terminal silica atoms have a maximum of three acyloxy groups and the non-terminal silicon atoms a maximum of two acyloxy groups.

Suitably, the poly(silyl ester)s comprising a structural unit of formula (I) will terminate with the groups $-\text{SiR}_1\text{R}_2\text{R}_3$ and $-\text{O}-\text{C}(\text{O})-\text{R}_7$.

In cases wherein m is greater than 2, i.e. in cases where the polyacid contains more than 2 $(\text{Z}(\text{O})\text{OH})$ groups, then L in formula (I) will have attached thereto the $(\text{Z}(\text{O})\text{OH})$ groups in excess of 2, and therefore polymerisation with the polyacyloxysilyl derivative can further occur from this/these additional $(\text{Z}(\text{O})\text{OH})$ sites.

Preferably, wherein R^1 , R^2 , R^4 and R^5 are alkoxy, aryloxy, alkaryloxy or hydroxyl in formula (III), they may represent $-\text{O}-\text{C}(\text{O})-\text{L}-$ in formula (I).

Preferably, R_4 and R_5 each independently represent an alkyl, an alkoxy, an aryl, an hydroxyl group or an $-\text{L}'-(\text{SiR}_4\text{R}_5\text{L}')_n-\text{SiR}_4\text{R}_5-$ group, wherein L' , R_1 , R_2 , R_4 and R_5 are as defined above and wherein preferably, $n=0-100$ and more preferably, $n=0-10$, most preferably $n=0$ but is also possibly 1, 2, 3, 4 or 5, preferably 1.

More preferably, R_4 and R_5 in formula (III) are each independently selected from the group comprising an alkyl

10

group, an hydroxyl group, an alkoxy group or an $-L'-(SiR_4R_5L')_n-SiR_1R_2-$ group, wherein L' , R_1 , R_2 , R_4 and R_5 are as defined above. Most preferably, R_1 , R_2 , R_4 and R_5 each independently represent an alkyl group. The said alkyl
5 groups may be branched or linear.

Preferably L' represents O.

Preferably Z represents C, POH, P or S=O, more preferably,
10 C.

According to an embodiment of the present invention, R_1 , R_2 , R_4 , R_5 and R_8 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl,
15 isobutyl, n-butyl, sec-butyl, t-butyl, phenyl, and vinyl. Preferably R_1 , R_2 , R_4 and R_5 are selected from the group consisting of methyl, ethyl, isopropyl, phenyl, and vinyl. More preferably, R_1 , R_2 , R_4 , R_5 and R_8 are methyl.

20 Preferably, the groups R_1 and R_2 are the same. Equally preferably, the groups R_7 and R_9 are the same, more preferably an alkyl group, most preferably methyl.

Preferably, R_7 and R_9 each represent an alkyl group, more
25 preferably methyl.

Preferably, R_6 is alkyl, most preferably methyl.

When R_4 and R_5 are alkoxy, they are preferably C_1 - C_4 oxy groups which may be branched or linear, more preferably,
30 C_1 - C_4 oxy groups, most preferably, a methoxy group.

11

Preferably, when R_4 or R_5 is selected as $-L'-(SiR_4R_5L')_n-SiR_1R_2-$, the R_4 and R_5 groups attached to the silicon radical in the selected group are not themselves, $-L'-(SiR_4R_5L')_n-SiR_1R_2-$.

5

Preferably, n as used herein each independently represent 0 to 500, more preferably 0 to 100, most preferably 0 to 10. Especially preferred values for n are selected from 0, 1, 2, 3, 4 or 5, most especially from 0 and 1.

10

The process of the invention enables one to obtain poly(silyl ester)s by reacting polyacids, preferably polycarboxylic acids, with polyacyloxysilyl derivatives.

- 15 The present invention relates to a new process for the synthesis of poly(silyl ester)s according to the general scheme whereby a polyacyloxysilyl derivative of formula (III), is reacted with a polyacid, preferably a polycarboxylic acid, of formula (II) and comprising at
20 least two acid groups, preferably two carboxylic acid groups, to form poly(silyl ester)s comprising a structural unit of formula (I).

- The reactants are mixed together either with or without
25 solvents. Preferably, the reaction is carried out in a suitable solvent. Suitable solvents which can be used in the process of the invention include non polar inert solvents, cyclic and non-cyclic aliphatic hydrocarbons, cyclic and non-cyclic ethers, esters, and the like.
30 Examples of suitable solvents which can be used in the process according to the invention include pentane, cyclopentane, hexane, cyclohexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane,

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decahydronaphthalene, diethyl ether, diisopropyl ether, diisobutyl ether, N,N-dimethylformamide, N-methylpyrrolidone, N,N-dimethylacetamide, and the like and mixtures thereof.

5

Preferred solvents are those which cause no distillation of any of the reactants, especially those solvents which allow preferential distillation of one of the products. Thus, a more especially preferred solvent is a solvent
10 which forms a low boiling azeotrope with the distilled acid product of the process of the invention. Still more especially preferred solvents are those which form a heterogeneous low boiling azeotrope with the distilled acid product.

15

More preferably, the solvents are independently selected from pentane, hexane, cyclohexane, heptane, toluene and xylene.

20 Preferably, the temperature of the reaction depends on the boiling point of the acid or its azeotrope that has to be distilled; the shape of the reactor and the height of the distillation column.

25 Typically, the reaction is carried out in the range 0°C - 200°C, more preferably, 60-190°C, most preferably, 110-180°C.

Preferably, the molar ratio of the reactive groups present
30 in the polyacyloxysilyl derivative and the polyacid is between 1:100 and 100:1, more preferably between 10:1 and 1:10, most preferably, between 2:1 and 1:2. Preferably,

13

the molar ratio of acyloxy group:acid group is approximately 1:1.

Preferably, the solvent, where present, is at least 10 wt% of the total reaction mix at the start of the reaction, more preferably, at least 20 wt%, most preferably, at least 30 wt%. The reaction may be carried out at atmospheric pressure although both higher and lower pressures are also possible.

10

The reaction may also be performed without solvent and accordingly suitable ranges of solvent are 0-99 wt% of the total reaction mix, more preferably, 20-50 wt%, most preferably 30-40 wt%.

15

In a preferred embodiment, L represents an alkyl, aryl, alkenyl, alkynyl, or aralkyl radical, or a polymer, preferably comprising 1 to 10000 carbon atoms, more preferably 1 to 1000 carbon atoms, most preferably 1 to 100 carbon atoms.

20

In a further preferred embodiment, L represents $-(CH_2)_n-$, wherein n is an integer between 1 and 10, preferably between 2 and 8, more preferably between 4 and 6, most preferably 4, or L represents a lactic acid or rosin residue, for example the non-carboxylic acid portions, or portions minus two of the carboxylic acid groups present, of a polylactic or substituted polylactic acid, e.g. dilactic acid, rosin and/or rosin derivatives, e.g. DYMEREX® (rosin dimer).

30

The reaction progress may be monitored by any suitable analytical method as well as with the determination of the amount of acid distilled.

5 Although any dicarboxylic or, more generally, polycarboxylic acid, or even polyacid, of formula (II) may be used in the process according to the invention, dicarboxylic acids are preferred, and preferred examples of dicarboxylic acids are adipic acid, oxalic acid,
10 succinic acid, glutaric acid, phthalic or isophthalic or terephthalic acids, and the like, a polylactic acid such as di-lactic acid, and rosinous dicarboxylic acids such as DYMEREX[®] (rosin dimer). Moreover, formula (II) may represent a polymeric polyacid.

15

The polyacyloxysilyl derivatives which can be used in the process according to the invention are preferably those derived from carboxylic acids having a boiling point of maximum 162°C, preferably of maximum 140°C, more
20 preferably of maximum 120°C, in order to facilitate the removal of the product after the transesterification. Examples of suitable carboxylic acids are formic acid, acetic acid, propionic acid and butyric acid. Formic acid and acetic acid with respectively 100°C and 118°C as
25 boiling points are preferred, with acetic acid being particularly preferred.

In another embodiment of the invention the polyacyloxysilyl derivatives are derived from partially or
30 totally halogenated acids, preferably from fluorinated or chlorinated acids, more preferably from trifluoroacetic acid with 70°C as boiling point.

The polyacyloxysilyl derivatives for use in the process of the invention are known (see table) or can be obtained by known methods. Some non-limiting examples are given in the following table:

5

polyacyloxysilyl derivative	CAS registry number
tetramethyl-1,3- diacetoxysiloxane	5314-58-9
dimethyldiacetoxysilane	2182-66-3
diethyldiacetoxysilane	18269-81-3
diphenyldiacetoxysilane	2566-07-3
vinylmethyldiacetoxysilane	2944-70-9
methyltriacetoxysilane	4253-34-3
ethyltriacetoxysilane	17689-77-9
vinyltriacetoxysilane	4130-08-9
phenyltriacetoxysilane	18042-94-1
tetraacetoxysilane	562-90-3
butanolic acid, 1,3,5-triethyl-1,3,5-tripropyl-1,5-trisiloxanediyl ester	34740-39-1
1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, dipropionate	34732-57-5
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(7-hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxanoxy)-, diacetate	33002-43-6
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(5-hydroxy-1,1,3,3,5,5-hexamethyltrisiloxanoxy)-, diacetate	33002-42-5
2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(3-hydroxy-1,1,3,3-tetramethyldisiloxanoxy)-, diacetate	33002-41-4
1,9-pentasiloxanediol, 1,3,5,7,9-pentamethyl-1,3,5,7,9-pentavinyl-, diacetate	23174-06-3
1,7-tetrasiloxanediol, 1,3,5,7-tetraethenyl-1,3,5,7-tetramethyl-, diacetate	23174-05-2
1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octaethyl-, diacetate	23174-10-9
1,5-trisiloxanediol, 1,3,5-triethenyl-1,3,5-trimethyl-, diacetate	23174-04-1
heptasiloxane, 1,1,1,13-tetraacetoxy-3,3,5,5,7,7,9,9,11,11,13,13-dodecamethyl	22306-76-9
1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-trimethyl-, diacetate	21982-13-8
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dibutyrate	21961-88-6
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dipropionate	21961-87-5

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1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, diacetate	21961-86-4
1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, diacetate	21961-85-3
1,1,1,7-tetrasiloxanetetrol, 3,3,5,5,7,7-hexamethyl-, triacetate	19363-46-3
1,5-trisiloxanediol, 1,1,3,5,5-pentamethyl-3-vinyl-, diacetate	18038-26-1
1-tetrasiloxanol, 7-acetyl-1,1,3,3,5,5,7,7-octamethyl-, acetate	6990-26-7
1-pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate; pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate	6904-56-9
1,9-pentasiloxanediol, decamethyl-, diacetate	5314-51-4
1,5-trisiloxanediol, hexamethyl-, diacetate	5314-52-0
1,17-nonasiloxanediol, octadecamethyl-, diacetate	3527-48-8
1,15-octasiloxanediol, hexadecamethyl-, diacetate	3454-14-6
1,7,13-heptasiloxanetriol, tridecamethyl-, triacetate	3293-05-8
1,1,7-tetrasiloxanetriol, 1,3,3,5,5,7,7-heptamethyl-, triacetate	3293-04-7
1,13-heptasiloxanediol, tetradecamethyl-, diacetate	3293-03-6
1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octamethyl-, diacetate	3293-02-5

Suitably, there is no limit on the molecular weight of the final product. However, the molecular weight is preferably in the range 1000 to 1000000 kD, more preferably 1000 to 100000 kD, most preferably 1000 to 10000 kD.

As used herein, the term "polymer" refers to the product of a polymerisation reaction, and is inclusive of homopolymers, copolymers, e.g. polysilanol, polyols, polyamines, etc. (which can react/esterify with the polyacid and/or polyacyloxysilanes; in the case of polysilanol, the non-hydrolysable Si-O bond will be part of the polymer), terpolymers, etc.

15

As used herein, the term "independently selected" or "independently represent" indicates that each radical, e.g. R, so described, can be identical or different.

5 The term "alkyl", as used herein and unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms more preferably 1 to 8
10 carbon atoms, still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Said radicals may be substituted, i.e. optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of
15 such radicals include and may be independently selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, iso-amyl, n-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl,
20 and the like.

The term "alkynyl", as used herein, relates to hydrocarbon radicals having one or several triple bonds, having straight, branched, polycyclic or cyclic moieties or
25 combinations thereof and having from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably from 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkynyl radicals include ethynyl, propynyl,
30 (propargyl), butynyl, pentynyl, hexynyl and the like.

The term "aryl", as used herein and unless otherwise defined, relates to an organic radical derived from an

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aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and the like.

20

The term "alkenyl", as used herein and unless otherwise defined, relates to hydrocarbon radicals having one or several double bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Said radicals may be substituted, i.e. optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl,

cyclohexenyl, 1-propenyl, 2-butenyl, 2-methyl-2-butenyl, isopenyl, farnesyl, geranyl, geranylgeranyl and the like.

The term "aralkyl", as used herein and unless otherwise
5 defined, relates to a group of the formula alkyl-aryl, in
which alkyl and aryl have the same meaning as defined
above. Said radicals may be substituted, i.e. optionally
substituted with one or more substituents independently
selected from alkyl, alkoxy, halogen, hydroxy or amino
10 radicals. Examples of aralkyl radicals include benzyl,
phenethyl, dibenzylmethyl, methylphenylmethyl, 3-(2-
naphthyl)-butyl, and the like.

Examples of the or each carboxyl radical part of formula
15 (III), $R_1C(O)$, $R_2C(O)$ and $R_3C(O)$, may include but are not
limited to formyl, acetyl, propionyl, butyryl, pivaloyl,
oxaloyl, malonyl, succinyl, glutaryl, adipoyl, benzoyl,
phthaloyl, isobutyroyl, sec-butyroyl, octanoyl,
isooctanoyl, nonanoyl, isononanoyl, abietyl,
20 dehydroabietyl, dihydroabietyl, naphthenyl, anthracenyl,
abietyl dimer (DYMEREX[®]), dihydroabietyl (FORAL[®]) and the
like and polymers or copolymers thereof. In a preferred
embodiment, said carboxyl radical parts are formyl,
acetyl, propionyl or butyryl. Most preferably, the
25 carboxyl radical part is acetyl.

The advantage of the process of the invention is that the
process uses reactants which can be easily handled, are
relatively inexpensive, and do not result in the emission
30 by distillation of any harmful products. Indeed, only
harmless and easily distillable acids, for example
carboxylic acids, are released, thus allowing for the
degree of conversion of the starting materials to the

target products to be monitored by conventional analytical tools and/or by determining the amount of distilled carboxylic acid released. A further advantage is that the formed acid(s), e.g. carboxylic acids, may be removed, preferably, under distillation, preferably azeotropic distillation. A yet further advantage is that the reaction proceeds either with or without a solvent present. Moreover, the process proceeds at an acceptable rate without the need for any added catalyst. Overall, due to the simplicity and shortness, its easy work-up procedure and its high yield, the process of the present invention can be considered as a significant and substantial improvement over the existing methods. In addition, the claimed synthesis route can be carried out at high temperatures and is therefore quick and efficient.

As noted above, the polymers formed by the process of the invention have a broad range of applications wherever there is the need for hydrolysable poly(silyl ester)s groups. The polymers thus formed exhibit a variable but predictable degradation behaviour and as such, have many potential applications. For instance, degradable polymers have previously been used in the medical and environmental fields in view of the fact they can be synthesised with the requisite physical and mechanical properties to firstly perform a given function and then break down into biologically or environmentally resorbable small-molecule byproducts. In the medical field, the nature of the side-group on degradable polymers can create functional materials having the ability to bind to specific sites, and so on.

21

Therefore, according to a second aspect of the present invention, there is provided an antifouling coating composition comprising a poly(silyl ester) as prepared by the process hereinbefore defined.

5

Moreover, and according to a third aspect of the present invention, there is provided a poly(silyl ester) as prepared by the process hereinbefore defined.

10 Finally, certain of the poly(silyl ester)s hereinbefore disclosed are themselves novel and form a further aspect of the present invention.

Thus, according to a fourth aspect of the present
15 invention, there is provided a poly(silyl ester) compound comprising the repeating group of general formula (I) hereinbefore defined, and wherein L is a polylactic acid or substituted polylactic acid residue or a rosin or substituted rosin residue of a polycarboxylic acid.

20

The second, third and fourth aspects of the present invention may incorporate any one or more of the preferred features of the first aspect of the invention except where such features are mutually exclusive.

25

The invention will now be described by way of illustration only and with reference to the accompanying non-limiting examples and attached drawings.

30

Examples and Comparative ExamplesPreparative Example

5 1,3-diacetoxytetraaisopropyldisiloxane was prepared in an analogous manner to that method disclosed by Volkova et al (see, Bull.Acad.Sci. USSR Div.Chem.Sci. (1963) 1829). Specifically, 250g of 1,3-dichlorotetraaisopropyldisiloxane (CAS No. 69304-37-6) and 282 9g of acetic anhydride were
10 heated to about 138-146°C, whilst acetyl chloride was gently distilled off. Vacuum distillation furnished unreacted acetic anhydride and 266.2g of 1,3-diacetoxytetraaisopropyldisiloxane (106°C, 0.6 mbar, 73%) as a colourless liquid.

15

IR (film) : 2951, 2873, 1731, 1466, 1371, 1261, 1244, 1099, 1018, 937, 886, 747, 695 cm^{-1} .

NMR data have been determined in CDCl_3 and are expressed
20 as delta versus TMS.

^{13}C NMR : 170.3, 22.2, 16.8, 13.0; ^{29}Si NMR: -11.8.

Example 1

25

40g of 1,3-diacetoxytetraaisopropyldisiloxane, prepared as described in the Preparative Example above, and 16.06g of adipic acid were heated at about 145-180°C, whilst acetic acid was distilled out of the reactor over 6 hrs. A
30 polymer with a solid content of 96.1%, a molecular weight of 4000 D (4 kD) and a viscosity of 80 dPa.s was obtained. The molecular weight decrease of a THF solution was

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monitored by GPC, as shown in Figure 1 of the attached drawings.

NMR data have been determined in CDCl_3 and are expressed
5 as delta versus TMS.

^{13}C NMR : 172.8, 35.6, 24.7, 17.0, 13.1; ^{29}Si NMR : -11.38.

Comparative Example 1 (according to Wooley et al,
10 Macromolecules (1998) 31 15)

1.1325g of bis(trimethylsilyl)adipate was reacted with
1.0318g of 1,1,3,3-tetraisopropyldisiloxane at 135°C for
14 days to produce poly(tetraisopropyldisilyl oxyl
15 adipate) with a molecular weight of 2700.

Example 2

263g of FORAL[®] AX-E (dihydroabietic acid) and 308g of
20 DYMREX[®] (rosin dimer) were placed in a 1.2 litre flask
equipped with a mechanical stirrer, a temperature control
and small column with cooler and receiver. The mixture
was melted by heating up to 220°C . Then 120g of
ethylsilyltriacetate was added and distillation of acetic
25 acid began at 155°C and ended at 175°C . The distillation
was continued under a reduced pressure of 150 mbar for 1
hour. 92g of acetic acid was distilled off, representing
101% of the acid that can be generated. The remaining
resin was dissolved with 400g of xylene and then cooled to
30 ambient temperature. The solid content of the product was
60%.

24

The binder solution had a viscosity of 1 dPa.s at a solid content of 60%. A drawdown of the resin solution on a glass plate showed the next day a dry/clear film. The binder film developed a light haze upon immersion in water
5 for 24 hours, but otherwise, did not show any significant changes with time. The film was then exposed to an alkaline solution of NaOH (pH value of 12.3) and exhibited hydrolysis and erosion at the surface, dissolving completely within one hour.

10

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and
15 which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification
20 (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

25

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated
30 otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

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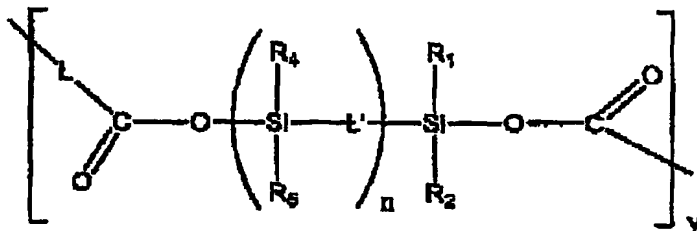
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any
5 accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

26

CLAIMS

1. A process for the preparation of poly(silyl ester)s comprising a structural unit of the formula (I)

5



(I)

wherein each R_4 and R_5 may be hydroxyl or may be
 10 independently selected from alkyl, aryl, alkoxyl, aryloxy, $-L'-SiR_1R_2-$, $-L'-(SiR_4R_5L')_n-SiR_1R_2-$, alkenyl, alkynyl, aralkyl or aralkyloxy radicals optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl,
 15 aralkyl, aralkyloxy, hydroxyl, aryl, aryloxy, halogen, amino (preferably, tertiary amino) or amino alkyl radicals, or R_4 or R_5 may independently be an $-O-C(=O)-L-$ group,

20 wherein each R_1 and R_2 may independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxy, aralkyl or aralkyloxy radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl,
 25 aralkyl, aralkyloxy, aryl, aryloxy, halogen, hydroxyl, amino (preferably, tertiary amino) or amino alkyl radicals, or R_1 or R_2 may independently be an $-O-C(=O)-L-$ group,

27

wherein L represents a hydrocarbyl or substituted hydrocarbyl group, wherein said substituted hydrocarbyl is substituted by one or more substituents independently
 5 selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxy, aryl, aryloxy, hydroxyl, halogen, amino or amino alkyl radicals, or a polymer with pendant acid groups,

10 L' represents O, S, or NR₆, where R₆ is defined as is R₇ below, or L,

each n independently represents a number of -Si(R₄)(R₅)-
 L'- groups from 0 to 1000,

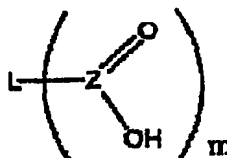
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and y represents a number of silyl ester repeat units from
 2 to 100000,

which process comprises the step of reacting;

20

a polyacid of formula (II)



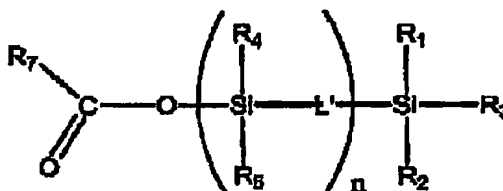
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(II)

wherein Z(O)OH represents the acid moiety attached to L, m
 is an integer from 2 to 100000, and L is as defined above,
 with a polyacyloxysilyl derivative of formula (III)

30

28



(III)

5 wherein R_1 , R_2 , R_4 , R_5 , L' and n are as defined above,
 except R_1 , R_2 , R_4 and R_5 in (III) are $-\text{O}-\text{C}(\text{O})-\text{R}_6$, where R_6
 is defined as is R_7 below, when the equivalent group in
 (I) is $-\text{O}-\text{C}(\text{O})-\text{L}-$, and R_7 is a hydrogen atom, an aralkyl,
 aryl, alkenyl, alkynyl, or alkyl group optionally
 10 substituted with one or more substituents selected from
 the equivalent substituents as defined for R_1 , R_2 , R_4 and
 R_5 above,

and R_3 is the group $-\text{O}-\text{C}(\text{O})-\text{R}_9$, where R_9 is defined as is
 15 R_7 above,

whilst removing the formed acid group(s) of formula (IV)
 and (V),

20 R_7 $\text{Z}(\text{O})\text{OH}$ (IV),

R_9 $\text{Z}(\text{O})\text{OH}$ (V),

from the system.

25

2. A process according to claim 1, wherein y is 2 to
 1000.

3. A process according to either of claims 1 and 2,
wherein R_4 and R_5 each independently represent an
alkyl, an alkoxy, an aryl, an hydroxyl group or an
-L'-(Si R_4R_5L') $_n$ -Si R_1R_2 - group, wherein L', R_1 , R_2 , R_4
5 and R_5 are as defined in claim 1.
4. A process according to claim 3, wherein $n = 0-100$.
5. A process according to claim 3, wherein $n = 0-10$.
- 10 6. A process according to claim 3, wherein n is 0 or 1.
7. A process according to any preceding claim, wherein
 R_4 and R_5 in formula (III) are each independently
15 selected from the group comprising an alkyl group, an
hydroxyl group, an alkoxy group or an
-L'-(Si R_4R_5L') $_n$ -Si R_1R_2 - group, wherein L', R_1 , R_2 , R_4
and R_5 are as defined in claim 1.
- 20 8. A process according to claim 7 wherein R_1 , R_2 , R_4 and
 R_5 each independently represent an alkyl group,
branched or linear.
9. A process according to any preceding claim, wherein
25 L' represents O.
10. A process according to any preceding claim, wherein Z
represents C, POH, P or S=O.
- 30 11. A process according to claim 1, wherein R_1 , R_2 , R_4 , R_5
and R_6 are each independently selected from the group
comprising methyl, ethyl, propyl, isopropyl,

isobutyl, n-butyl, sec-butyl, t-butyl, phenyl, and vinyl.

- 5 12. A process according to claim 11, wherein R_1 , R_2 , R_4 and R_5 are selected from the group consisting of methyl, ethyl, isopropyl, phenyl, and vinyl.
- 10 13. A process according to claim 11, wherein R_1 , R_2 , R_4 , R_5 and R_6 are methyl.
- 14 14. A process according to any preceding claim, wherein R_6 is methyl.
- 15 15. A process according to any preceding claim, wherein the groups R_1 and R_2 are the same.
- 16 16. A process according to any preceding claim, wherein the groups R_7 and R_8 are the same.
- 20 17. A process according to claim 16, wherein R_7 and R_8 are alkyl.
- 25 18. A process according to claim 16, wherein R_7 and R_8 are methyl.
- 30 19. A process according to claim 1, wherein the polyacid of formula (II) is a polycarboxylic acid.
20. A process according to claim 19, wherein the polycarboxylic acid is a dicarboxylic acid.
21. A process according to any preceding claim, wherein L represents an alkyl, aryl, alkenyl, alkynyl, or

aralkyl radical, or a polymer, preferably comprising 1 to 10000 carbon atoms.

22. A process according to claim 1, wherein L represents
5 $-(CH_2)_n-$, and n is an integer between 2 and 8.

23. A process according to claim 20, wherein the
dicarboxylic acid is selected from adipic acid,
oxalic acid, succinic acid, glutaric acid, phthalic
10 or isophthalic or terephthalic acids, di-lactic acid,
and rosinous dicarboxylic acids.

24. A process according to claim 1, wherein the
polyacyloxysilyl derivatives of formula (III) are
15 selected from tetraisopropyl-1,3-
diacetoxysiloxane, tetramethyl-1,3-
diacetoxysiloxane, dimethyldiacetoxysilane,
diethyldiacetoxysilane, diphenyldiacetoxysilane,
vinylmethyldiacetoxysilane, methyltriacetoxysilane,
20 ethyltriacetoxysilane, vinyltriacetoxysilane,
phenyltriacetoxysilane, tetraacetoxysilane,
(butanoic acid, 1,3,5-triethyl-1,3,5-tripropyl-1,5-
trisiloxanediyl ester), (1,5-trisiloxanediol, 1,3,5-
triethyl-1,3,5-tripropyl-, dipropanoate),
25 (2-silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(7-
hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxanoxy)-,
diacetate), (2-silanaphthalen-2-ol, 1,2,3,4-
tetrahydro-2-(5-hydroxy-1,1,3,3,5,5-
hexamethyltrisiloxanoxy)-, diacetate), (2-
30 silanaphthalen-2-ol, 1,2,3,4-tetrahydro-2-(3-hydroxy-
1,1,3,3-tetramethyldisiloxanoxy)-, diacetate), (1,9-
pentasiloxanediol, 1,3,5,7,9-pentamethyl-1,3,5,7,9-
pentavinyl-, diacetate),

(1,7-tetrasiloxanediol, 1,3,5,7-tetraethenyl-1,3,5,7-tetramethyl-, diacetate), (1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octaethyl-, diacetate), (1,5-trisiloxanediol, 1,3,5-triethenyl-1,3,5-trimethyl-, diacetate), (heptasiloxane, 1,1,1,13-tetraacetoxy-3,3,5,5,7,7,9,9,11,11,13,13-dodecamethyl), (1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-trimethyl-, diacetate), (1,5-trisiloxanediol, 1,1,3,3,5,5,-hexaethyl-, dibutyrate), (1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, dipropionate), (1,5-trisiloxanediol, 1,3,5-triethyl-1,3,5-tripropyl-, diacetate), (1,5-trisiloxanediol, 1,1,3,3,5,5-hexaethyl-, diacetate), (1,1,1,7-tetrasiloxanetetrol, 3,3,5,5,7,7-hexamethyl-, triacetate), (1,5-trisiloxanediol, 1,1,3,5,5-pentamethyl-3-vinyl-, diacetate), (1-tetrasiloxanol, 7-acetyl-1,1,3,3,5,5,7,7-octamethyl-, acetate), (1-pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate; pentasiloxanol, 9-acetyl-1,1,3,3,5,5,7,7,9,9-decamethyl-, acetate), (1,9-pentasiloxanediol, decamethyl-, diacetate), (1,5-trisiloxanediol, hexamethyl-, diacetate), (1,17-nonasiloxanediol, octadecamethyl-, diacetate), (1,15-octasiloxanediol, hexadecamethyl-, diacetate), (1,7,13-heptasiloxanetriol, tridecamethyl-, triacetate), (1,1,7-tetrasiloxanetriol, 1,3,3,5,5,7,7-heptamethyl-, triacetate), (1,13-heptasiloxanediol, tetradecamethyl-, diacetate), and (1,7-tetrasiloxanediol, 1,1,3,3,5,5,7,7-octamethyl-, diacetate).

25. A process according to any preceding claim, wherein the reaction is carried out in a suitable solvent.
26. A process as claimed in claim 25, wherein the solvent
5 is selected from pentane, cyclopentane, hexane, cyclohexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthalene, diethyl ether, diisopropyl ether, diisobutyl ether, N,N-dimethylformamide, N-methylpyrrolidone,
10 N,N-dimethylacetamide, and mixtures thereof.
27. A process according to either of claims 25 and 26, wherein the solvent forms a heterogeneous low boiling
15 azeotrope with the distilled acid product.
28. A process according to any preceding claim, wherein the molar ratio of the reactive groups present in the polyacyloxysilyl derivative:acid is between 1:100 and
20 100:1.
29. A process according to any preceding claim, wherein the solvent, where present, is at least 10 wt% of the total reaction mix at the start of the reaction.
25
30. A process according to any preceding claim, wherein the molecular weight is in the range 1000 to 1000000 kD.
- 30 31. A process according to claim 30, wherein the molecular weight is in the range 1000 to 100000 kD.

34

32. A process according to claim 30, wherein the molecular weight is in the range 1000 to 10000 kD.
33. A process according to any preceding claim, wherein m
5 is 2.
34. A process according to any one of claims 1 to 33 which includes the additional step of incorporating the polymer in a film or coating composition.
10
35. A process for the preparation of poly(silyl ester)s as hereinbefore described and with reference to the examples and figure.
- 15 36. An antifouling coating or film composition comprising a poly(silyl ester) as prepared by a process in accordance with any of claims 1 to 33.
- 20 37. A film or coating comprising a polymer as prepared by a process as defined in any of claims 1 to 33.
38. A poly(silyl ester) as prepared by a process as defined in any one of claims 1 to 33.
- 25 39. A poly(silyl ester) comprising the repeating group (I) as defined in claims 1 to 33, and wherein L is a polylactic acid or substituted polylactic acid residue or a rosin or substituted rosin residue of a polycarboxylic acid.
- 30

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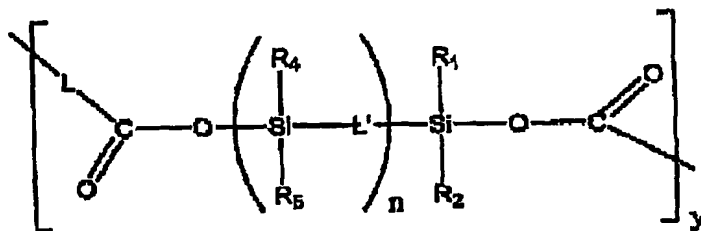
ABSTRACT

PROCESS FOR THE PREPARATION OF POLY(SILYL ESTER)S,
AND THEIR USES

5

The present invention provides a process for the preparation of poly(silyl ester)s comprising a structural unit of the formula (I)

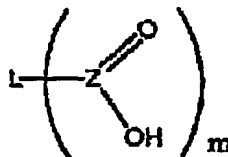
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(I)

15 which process comprises the step of reacting;

a polyacid of formula (II)

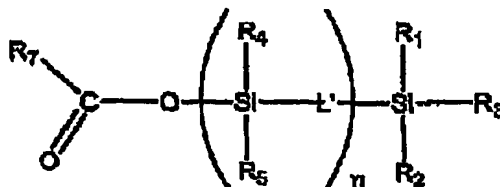


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(II)

36

with a polyacyloxysilyl derivative of formula (III)



5

(III)

whilst removing the formed acid group(s) of formula (IV)
and (V),

10

$\text{R}_7 \text{ Z(O)OH (IV),}$

$\text{R}_9 \text{ Z(O)OH (V).}$

15 from the system.

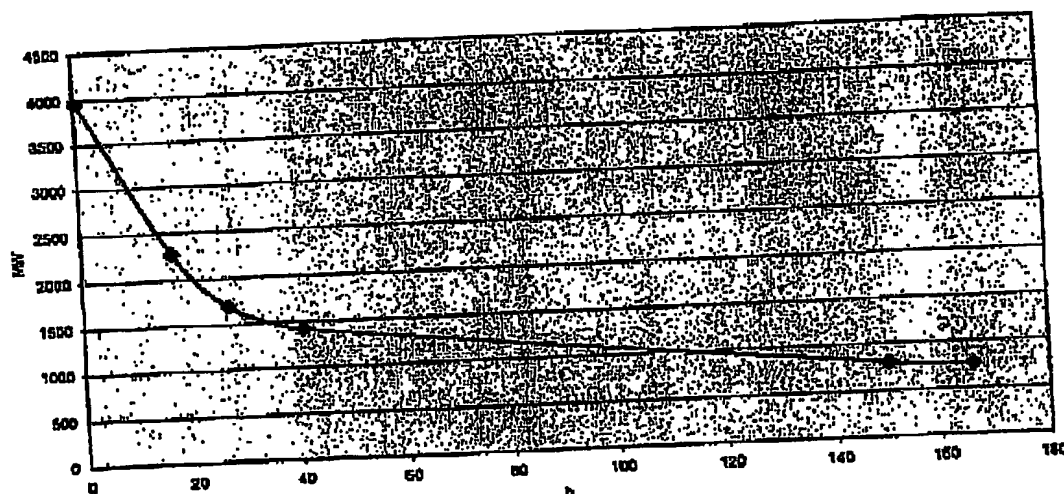


Figure 1

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PCT/EP2004/003258



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